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(54) **Composite separation membranes**

(57) Synthetic, organic, polymeric membranes are prepared by applying to a microporous support an aqueous solution of a salt of polyacrylic acid, cross-linking by treating the surface with a cross-linking agent and heat curing.

GB 2 174 619 A

SPECIFICATION

Pervaporation separation of ethanol-water mixtures using polyacrylic acid composite m m-branes

BACKGROUND OF THE INVENTION
1. FIELD OF THE INVENTION
The invention generally relates to liquid purification or separation. More specifically, the invention relates to membrane materials for separation of ethanol and water mixtures. The invention also relates generally to coating processes in which a permselective product is produced, specifically a thin, dense coating on a microporous substrate.
2. DESCRIPTION OF THE PRIOR ART
Ethanol is commonly produced by fermentation processes, wherein the ethanol product is found in a water mixture. The production of fuel-grade ethanol requires that the fermentation product be dried beyond the azeotrope. The usual drying process of distillation requires a significant amount of energy. Therefore, it is desirable to separate ethanol from fermentation beers by a more economical method, such as by membrane separation. In addition, significant preferential passage of ethanol at feed concentrations corresponding to fermentation beers can be a significant result because it may permit a fermentation process to operate at a low ethanol concentration while yielding a pervaporate sufficiently enriched for further processing by distillation or other means.

Selective membranes have been used in reverse osmosis processes, such as in the desalination of seawater and the separation of azeotropic mixtures of aromatic and aliphatic hydrocarbons or close boiling isomers. A principal disadvantage of reverse osmosis is that a high pressure is needed in excess of the prevailing osmotic pressure to drive the permeate through the membrane. Pervaporation avoids the limitation of osmotic pressure imposed on reverse osmosis processes by maintaining the permeate below its saturated vapor pressure. The heat of vaporization must be supplied to the permeating fraction in pervaporation, whereas during reverse osmosis there is no phase change and the heat of vaporization is not required. Thus, membranes used in the pervaporation process must meet more stringent membrane performance. To minimize energy input, membranes that pass water selectively would be of importance for solutions concentrated in ethanol, while membranes that pass ethanol selectively could remove ethanol directly from a fermentation bath. In either of these concentration regimes, osmotic pressures would hinder the competitive use of reverse osmosis.

The membrane separation of ethanol from water is difficult, and those membranes used for the separation of ethanol from either simple aqueous mixtures or from fermentation beers using reverse osmosis or pervaporation have been successful usually only in achieving a permeate that is enriched in water. A small number of exceptions to this result have been noted in published literature, as follow. It is reported in Heisler, E.G., A.S. Hunter, J. Siciliano, R.H. Treadway, *Science*, Vol. 124, p. 77, 1956, that adding benzoic acid to the feed yielded a slight enrichment of ethanol in the permeate when used with a cellophane membrane. Eustache, H., and G. Histi, *J. Membr. Sci.*, Vol. 8, p. 105, 1981, report the use of pervaporation with a membrane of polydimethylsiloxane to yield a permeate enriched in ethanol. However, the latter measurements used feeds of only very low ethanol concentrations (ca. 0.1–1.0%). Finally, Hoover, K.C., and S. T. Hwang, *J. Membr. Sci.*, Vol. 10, p. 253, 1982, report the use of a silicone rubber membrane in a pervaporation column with good separation factors at low ethanol concentrations; however, there was essentially no separation at very high ethanol concentrations. Thus, the prior art has not produced a membrane that is well suited to the separation of ethanol from water over a wide range of concentrations.

A primary problem encountered in membrane technology used to separate ethanol from water mixtures remains the creation of a membrane material that optimizes the properties that permit high separation efficiency and permeability. Some of the factors that influence the permeation process in polymers include chemical composition, membrane homogeneity, and the imposed driving forces causing permeation. It remains unpredictable as to what membrane composition will best perform in these areas, as the mechanism or mechanisms of membrane separation remain somewhat controversial, although the general sorption-diffusion theory is supported by a growing body of evidence.

The efficiency of liquid permeation separations through polymer films depends primarily on whether there is an interaction, chemical or physical, between the solvent, solute, and polymer. The extent of the liquid-polymer interaction determines how swollen the polymer becomes. These interactions arise in general from polar-, steric-, nonpolar-, or ionic-character of each of the above three components in the membrane system. The overall result of their interactions determines whether solvent, solute, or neither is preferentially sorb d at the membrane-solution int rface.

Further, it has been observed that the permselectivit of a polymeric material increases as the

general level of flux rate decreases. This aspect of transport behavior must be overcome for
economic separation processes by appropriate changes in membrane geometry and by adjusting
polymer composition, structure, and morphology to enhance transport behavior of the chosen
penetrant. Both the diffusion coefficient and solubility coefficient of a penetrant are quite sensi-
5 tive to minor variations in polymer composition and structure, which provides a possibility to   5
experimentally derive useful permselective membrane materials.
   Changes in membrane geometry are of great importance, as flux is inversely dependent on film
thickness, while permeability constants are independent of thickness. Consequently, a very thin
film can be highly permselective with excellent overall fluxes of the desired penetrant species.
10 However, the presence and damaging effects of pinholes or other defects increase with decreas-   10
ing membrane thickness. In order to develop optimum thin film materials, it is therefore essential
that the dependence of permeability on factors that control transport processes be understood.
   The above noted factors, among others, demonstrate the difficulty faced in the development
of a membrane having the combination of high selectivity and concurrent high flux of the
15 permeating species. To achieve the foregoing and other objects and in accordance with the   15
purpose of the present invention, as embodied and broadly described herein, the membrane and
method of manufacture of this invention may comprise the following.

   SUMMARY OF INVENTION
20   Against the described background, it is therefore a general object of the invention to provide a   20
permselective membrane for water/ethanol mixtures.
   Another general object of the invention is to provide a membrane adapted to separate water-
ethanol mixtures with a combination of high selectivity and concurrent high flux of the permeat-
ing species.
25   A more specific object is to provide a synthetic, organic, polymeric membrane that permeates   25
water over a wide range of feed compositions in order to obtain a more highly concentrated
water-ethanol solution.
   Another specific object is to provide a process for making a membrane capable of efficiently
permeating at least a portion of the water from a feed solution in pervaporation process.
30   Additional objects, advantages and novel features of the invention shall be set forth in part in   30
the description that follows, and in part will become apparent to those skilled in the art upon
examination of the following or may be learned by the practice of the invention. The object and
the advantage of the invention may be realized and attained by means of the instrumentalities
and in combinations particularly pointed out in the appended claims.
35   In a process for preparing a composite membrane capable of selectively permeating water   35
from a water-ethanol mixture, an aqueous solution is prepared of a synthetic, organic, polymeric
substance consisting of a salt of polyacrylic acid. Then, a microporous support member is
coated with the prepared aqueous solution for a predetermined time sufficient to deposit a
uniform coating of the polymeric substance on the support member. Thereafter, the surface of
40 the polymeric substance is cross-linked by treating the surface with a cross-linking agent for a   40
predetermined time, after which the membrane is heat-cured.
   According to another aspect of the invention, a permeation apparatus is provided, having a
microporous support member, a coating on the support member of a synthetic, organic, poly-
meric substance characterized by the presence of acrylic acid groups, and a partially cross-linked
45 surface network on the coating.   45

   DESCRIPTION OF THE PREFERRED EMBODIMENTS
   Synthetic organic polymeric membranes were developed that separate ethanol-water mixtures
over a wide range of ethanol-water feed compositions. The membranes are characterized by the
50 presence of a polymer group consisting of acrylic acid. In each case, the process of testing the   50
membranes involved contacting a liquid feed mixture of ethanol and water against one side of a
membrane and withdrawing at the second side a vapor phase mixture having a higher concentra-
tion of ethanol or water than was present in the feed mixture.
   Membrane performance was measured and calculated to determine relevant parameters relating
55 to performance with ethanol (e) or water (w). The diffusion flow or flux, J_w, of substance w 55
through a film is defined as the amount passing during a unit time through a surface of unit area
normal to the direction of flow.
   A separation factor SFa_w for substance w in a system of two penetrants in a pervaporation
process is defined as the ratio of the permeability constants of each penetrant in the membrane
60 when the downstream pressure is close to zero, according to the equation: 60

   $SFa_w = P_w/P_e$
   where P is the permeability constant for the respective substance w or e and is defined by the
product of the solubility coefficient and the diffusion coefficient for the respective substance.
65   An alternative separation factor SFb_w is defined as: 65

$SFb_w = p_w / f_w$

where p is the weight fraction of the substance *w* in the downstream phase (permeate) and f_w is
the weight fraction of the substance *w* in the upstream phase (feed). For a *w* selective mem-
5   brane, SFa_w will be greater than SFb_w.   5
The efficiency or productivity factor of a pervaporator equipped with a given *w*-selective
membrane can be derived to be proportional to the product:

$(SFb_w - 1)J$
10 where J is the permeate flux.   10
Efficient and selective polymeric membranes were prepared from acrylic acid by dissolving the
polymeric substance in water to a predetermined concentration, dip-coating a microporous sup-
port in the aqueous solution, applying a cross-linking agent to the treated support for a time
sufficient to achieve a predetermined degree of cross-linking in the membrane surface, and heat
15 curing.   15
The membrane support member was chosen for its ability to carry the polymeric membranes
without interfering with or contributing to the separation. A polysulfone film was selected as the
preferred support film, as an uncoated polysulfone film does not exhibit any selectivity in a
water-ethanol system and, due to its microporosity, has a large flux of about 50 L/m^2h.
20 The polymeric substances were dissolved in aqueous solution in order to obtain a desired film   20
thinness and uniformity by the dip-coating process. It has been found that concentrations of less
than about 2% by weight are suitable, with the preferred concentration being generally less than
about 1% for polyacrylic acid in order to produce a membrane that has the desired thinness and
uniformity. After the coating is applied to the support, a limited degree of cross-linking is
25 desired to establish a cross-linked polymeric coating over the surface of the supported mem-   25
brane structure. A suitable cross-linking agent such as toluene-2,4-diisocyanate in a hexane
solution may be used to achieve the limited cross-linking by an interfacial addition reaction.
Exposure for approximately one minute is adequate to achieve the desired cross-linked surface
on the polymeric film.
30 The composite membrane is cured after cross-linking by drying in an oven at a temperature   30
from 100°C to 150°C. The curing process also removes residual water and hexane from the
polymer and its supporting structure.
The membrane may be a simple disk or sheet of the membrane substance. However, other
forms of membrane may also be employed, such as hollow tubes and fibers. Various other
35 shapes and sizes are readily adaptable to commercial installations.   35
Synthetic organic polymeric membranes characterized by the presence of acrylic acid groups
were produced and evaluated. The membranes were prepared in different variations, as illus-
trated in the following examples:

40 *Example 1.*   40
Synthetic organic polymeric membranes characterized by the presence of acrylic acid groups
were prepared from the sodium salt of polyacrylic acid. Polyacrylic acid was treated with sodium
hydroxide to partially neutralize the acrylic acid groups, with 10% residual acid groups remaining.
The resulting compound, having a molecular weight of approximately 6000, was dissolved in
45 water to produce an aqueous 0.68% solution. A polysulfone support membrane was dip-coated   45
in the solution by soaking for 10 minutes to form a membrane of substantially uniform thick-
ness. Thereafter, the membrane was drained for one minute and then dipped into a 0.5% TDI
solution in hexane for one minute to generate cross-links through an interfacial film reaction. The
prepared membrane was then heat-cured in a convection oven at 150°C for one hour.
50 Membrane performance was evaluated in a pervaporation apparatus that consists of a constant   50
temperature bath and pump that circulates the feed through a radial-flow cell at a rate of about
1.4 L/min and with bath temperatures controlled to 0.1°C. The membrane is mounted on a
porous plate of stainless steel embedded in the membrane cell. A downstream compartment
consists of two parallel pumping stations that allow alternate sampling from cold traps. Five
55 centimeter diameter pumping lines connect to the lower surface of the membrane to ensure that   55
pressures downstream are well below the saturated vapor pressures even for membranes pass-
ing up to 170 L/m^2h. A thermocouple gauge located immediately downstream from the mem-
brane was used as a semiquantitive monitor of the permeate pressure. Resulting pervaporation
data are presented below in Table 1, Table 2, and Table 3 f r, respectively, 23°C, 33°C, and
60 43°C bath temperatures.   60

TABLE 1.　PERVAPORATION MEASUREMENTS, PAA MEMBRANE (T = 23°C)

Run No.	Ethanol w-fraction		Permeation			SFa_w	SFb_w	J	$(SFb_w - 1)J$
	Feed	Permeate	Vol. (mL)	Time (h)	Pressure (Torr)			(L/m²h)	
1	0.435	0.111	4	2	0.06	6.2	1.6	0.51	0.31
2	0.098	0.035	9	3	0.07	3.0	1.1	0.77	0.07
3	0.803	0.197	11	7	0.05	16.6	4.1	0.40	1.23
4	0.668	0.216	9.4	6	0.05	7.3	2.4	0.40	0.56
5	0.825	0.173	11.2	7	0.05	22.5	4.7	0.41	1.51
6	0.780	0.201	12.5	7	0.05	14.0	3.6	0.46	1.18
7	0.312	0.030	14.2	7	0.06	14.8	1.4	0.52	0.21
8	0.983	0.698	2.4	6.5	0.03	25.3	17.9	0.09	1.52
9	0.942	0.363	4.0	7	0.04	28.5	11.0	0.15	1.50
10	0	0	10.4	2	0.1	--	--	1.33	--

TABLE 2. PERVAPORATION MEASUREMENTS, PAA MEMBRANE (T = 33°C)

Run No.	Ethanol w-fraction		Permeation		Pressure (Torr)	SFa_w	SFb_w	J (L/m²h)	$(SFb_w-1)J$
	Feed	Permeate	Vol. (mL)	Time (h)					
11	0.075	0.011	8.2	2	0.08	7.3	1.1	1.05	0.10
12	0.796	0.191	14.4	5	0.06	16.5	4.0	0.73	2.20
13	0.669	0.163	17.2	6	0.08	10.4	2.5	0.73	1.10
14	0.822	0.184	10	3.5	0.07	20.6	4.6	0.73	2.63
15	0.777	0.183	20	7	0.07	15.5	3.4	0.73	1.97
16	0.286	0.034	15	4.75	0.08	11.5	1.4	0.81	0.32
17	0.981	0.702	4.3	9	0.04	22.0	15.8	0.12	1.80
18	0.943	0.394	9.1	7	0.04	25.2	10.5	0.33	3.15
19	0	0	17.1	3	0.1	--	--	1.45	--

TABLE 3. PERVAPORATION MEASUREMENTS, PAA MEMBRANE (T = 43°C)

Run No.	Ethanol w-fraction Feed	Permeate	Permeation Vol. (mL)	Time (h)	Pressure (Torr)	SFa_w	SFb_w	J (L/m²h)	$(SFb_w-1)J$
20	0.074	0.016	53	8	0.11	4.9	1.1	1.70	0.17
21	0.799	0.199	11.1	2.5	0.10	16.0	4.0	1.13	3.40
22	0.633	0.142	33	6	0.09	10.4	2.3	1.40	1.82
23	0.824	0.215	43.8	10	0.08	17.1	4.5	1.12	3.92
24	0.769	0.181	34	7	0.09	15.0	3.6	1.35	3.51
25	0.219	0.025	36.4	6	0.08	11.2	1.3	1.50	0.45
26	0.943	0.424	16.5	7	0.05	22.6	10.2	0.60	5.52
27	0	0	34	4	0.12	--	--	2.17	--

Analysis of the resulting data demonstrates that this membrane has a high water selectivity that increases with increasing feed concentration of ethanol. Membrane flux varies with temperature, increasing with the feed temperature. The permeability of water is decreased when ethanol is present.

5   The PAA membrane has a high efficiency over the entire concentration range. The productivity   5
parameter $(SFb_w-I)J$ generally increases with increasing ethanol feed concentration up to about 90% ethanol. Above this concentration, membrane efficiency seems to level off or decrease.

Example 2.

10   Synthetic polymeric membranes were prepared according to the techniques of Example 1, with   10
the addition of an immersion in a 9.2% by weight calcium chloride solution for 93 hours. The membranes were evaluated in a pervaporation apparatus and with procedures as described in Example 1. Resulting pervaporation data are presented below in Table 4.

TABLE 4. PERVAPORATION MEASUREMENTS, CALCIUM CHLORIDE TREATED PAA MEMBRANE

Run No.	Ethanol w-fraction		Permeation							
	Feed	Permeate	Vol. (mL)	Time (h)	Temp. ($^{\circ}$C)	Pressure (Torr)	SFa_w	SFb_w	J (L/m^2h)	$(SFb_w-1)J$
28	0.921	0.176	4.0	8	23	0.03	54.4	10.4	0.13	1.23
29	0.921	0.144	6.4	8	33	0.04	69.2	10.8	0.20	1.96
30	0.904	0.085	8.7	7	43	0.06	101.5	9.5	0.32	2.69

The data show an increase in water selectivity and a decrease in flux in comparison to the membranes discussed in Example 1. The high water selectivity is demonstrated, for example, by the permeate from a 9.6% by weight water feed composition, which becomes enriched to 92% water.

5   The foregoing is considered as illustrative only of the principles of the invention. Further, since numerous modifications and changes will readily occur to those skilled in the art, it is not desired to limit the invention to the exact construction and operation shown and described, and accordingly all suitable modifications and equivalents may be regarded as falling within the scope of the invention as defined by the claims that follow.

10

CLAIMS

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1.   A process for preparation of a composite membrane capable of selectively permeating
15 water from an ethanol-water mixture, comprising:
preparing an aqueous solution of a synthetic, organic, polymeric substance comprising a salt of polyacrylic acid;
coating a microporous support member with said prepared aqueous solution for a predetermined time sufficient to deposit a uniform coating of the polymeric substance on the support
20 member;
cross-linking the surface of said polymeric substance coating by treating the surface with a cross-linking agent for a predetermined time; and
heat curing said cross-linked membrane.

2.   The process of claim 1, wherein the concentration of said polymeric substance in the
25 aqueous solution is no more than 2%.

3.   The process of claim 2, wherein said coating step is by soaking said microporous support member in said aqueous solution for approximately ten minutes.

4.   The process of claim 3, further comprising, after soaking the support member, draining the support member for approximately one minute before applying said cross-linking agent.

30   5.   The process of claim 1, wherein said cross-linking agent is a solution of toluene-2,4-diisocyanate in hexane.

6.   The process of claim 1, wherein said cross-linking agent is approximately a 0.5% by weight solution of toluene-2,4-diisocyanate in hexane, and said predetermined time of exposure is approximately one minute.

35   7.   The process of claim 1, wherein said sodium salt of polyacrylic acid has approximately 10% residual acid groups and molecular weight of about 6000.

8.   The process of claim 7, wherein said heat curing step is conducted at approximately 150°C for about one hour.

9.   The process of claim 1, wherein said microporous support member comprises a polysul-
40 fone film.

10.   A permeation apparatus, comprising:
a microporous support member;
a coating on said support member of a synthetic, organic, polymeric substance characterized by the presence of acrylic acid chemical groups; and
45   a partially cross-linked surface network on said coating.

11.   The permeation apparatus of claim 10, wherein said acrylic acid coating has approximately 10% residual acid groups remaining and has a molecular weight of about 6000.

12.   The permeation apparatus of claim 10, wherein said apparatus is the product of the process comprising:
50   soaking said microporous support in an aqueous solution of the coating material for a time sufficient to deposit a uniform coating layer on the support;
removing drainable solution from the coated support; and
exposing the coated support to a cross-linking agent for a time sufficient to form a partially crosslinked surface network of the coating material.

55   13.   The permeation apparatus of claim 10, characterized by said apparatus being the product of the process wherein said aqueous solution is no more than about 2% of said synthetic, organic, polymeric substance.

14.   The permeation apparatus of claim 10, chara terized by said apparatus being the product of the process wherein said cross-linking agent is 0.5% by weight toluene-2,4-diisocyanate
60 applied to the surface of said coating for about 1 minute.

15.   The permeation apparatus of claim 10, chara terized by said apparatus being the product of the process further comprising, after forming said cross-linked surface network, applying heat in a, quantity and for a time sufficient to cure the network.

16.   The permeation apparatus of claim 10, characterized by said coating having the resultant
65 composition of one prepared by the process of a polysulfone support member being soaked for

approximately 10 minutes in an aqueous 0.67% by weight solution of the sodium salt of polyacrylic acid having about 10% residual acid groups and a molecular weight of about 6000; the coated member thereafter having cross-links generated by exposure for about 1 minute to 0.5% by weight toluene-2,4-diisocyanate in hexane; and followed by heat curing at about 150°
5 for approximately 1 hour.

17. The apparatus of claim 16, wherein before said cross-links are generated, said support member is drained for about 1 minute.

18. The method of separating an ethanol-water mixture through a membrane film, comprising:

providing a polymeric membrane film of polyacrylic acid groups supported on a microporous
10 member and having a partially cross-linked and heat-cured surface;

providing an ethanol-water feed solution on a first side of said membrane film;

applying a pressure differential between first and second sides of the membrane film sufficient to induce a diffusion flow of a permeate from the feed solution through the membrane; and

recovering residual product solution from the first side of the membrane film.

15 19. The method of claim 18, wherein said permeate comprises a relatively decreased weight fraction of ethanol as compared to the feed solution at substantially any water-ethanol concentration.

20. The method of claim 18, wherein said polymeric membrane film is formed by the process comprising:

20 soaking said microporous support in an aqueous solution of a coating material for a time sufficient to deposit a uniform coating layer on the support, wherein the coating material is characterized by the presence of polyacrylic acid in which the acrylic acid groups are partially neutralized such that about 10% residual acid groups remain and the resulting compound has a molecular weight of approximately 6000;

25 removing drainable solution from the coated support;

exposing the coated support to a cross-linking agent for a time sufficient to form a partially cross-linked surface network of the coating material; and

applying heat in quantity and for a time sufficient to cure the network.

21. The method of claim 20, wherein said aqueous solution is no more than about 2% by
30 weight acrylic acid groups.

22. The method of claim 21, wherein said cross-linking agent comprises 0.5% by weight toluene-2,4-diisocyanate applied to the surface of said coating for about 1 minute.

23. The method of claim 20, wherein said polymeric membrane film is formed by the process further comprising treating the heat-cured membrane with calcium chloride to increase
35 water selectivity in the permeate.

24. The method of claim 23, wherein the membrane is immersed in approximately a 9.2% solution by weight calcium chloride for a time sufficient to increase water selectivity in the permeate.